UNITED STATES DEPARTMENT OF COMMERCE
Maurice H. Stans, Secretary
NATIONAL BUREAU OF STANDARDS • Lewis M. Branscomb, Director


# TECHNICAL NOTE 584

ISSUED DECEMBER 1971

Nat. Bur. Stand. (U.S.), Tech. Note 584, 175 pages (December 1971)
CODEN: NBTNA

# Analytical Coordination Chemistry Section:

## Summary of Activities July 1970 to June 1971

O. Menis and J. I. Shultz, Editors

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# 1. SPECTROPHOTOMETRY

## A. Introduction

During the past year considerable progress was made in the three-pronged program outlined in last year's progress report. These efforts included the construction and measurements with the high accuracy spectrophotometer, development and certification of glass filters for use in the calibration of the photometric scale in the visible region of the spectrum, and studies with liquid filters for checking the accuracy of spectrophotometric measurements which will be useful in automated clinical measurements. Last year's report discussed extensively the overall philosophy, need and the justification for the various approaches that were contemplated. The current report covers the details of the construction of the new high accuracy spectrophotometer, its calibration, and its application to the certification of Standard Reference Material 930, Glass Filters. These filters are suitable for calibrating the photometric scale in the region of the spectrum from 400 nm to 700 nm. The report also describes new studies leading to more accurate molar absorptivity values of the acid dichromate system and further progress in the development of spectrally neutral liquid filters.

Significant advances have been made in providing the basis for more accurate spectrophotometric measurements. The NBS single beam spectrophotometer now provides transmittance accuracy of at least 3 parts per thousand based on the stability of its components and an independent physical measurement of the linearity of transmittance. The accuracy value of 0.5 percent relative standard deviation assigned to the SRM 930, Glass Filter, is limited at present by the quality of the material.

A restudy of the acid dichromate systems led to a tenfold improvement in the values for the equilibrium

formation of the dichromate dimer and provides a basis for measurement and recalculating of the molar absorptivity of the complex in the visible and UV regions of the spectrum and to provide flexible systems for calibrating multielement analysis in automated systems.

A major need is to improve the accuracy of the data being collected in the field of clinical chemistry. In addition to standards, improved methodology is needed to attain higher accuracy in this field. The present efforts in the area of standardization need to be extended to include stray light, bandpass, cell path calibrations, and ultimately a definite Standard Reference Material incorporating the multicomponent material of interest in health or pollution problems. To focus on the overall problem, a conference on Spectrophotometry and Luminescence Analysis has been planned for March 22-24, 1972 at NBS. Papers will be presented by experts in these measurement areas and also by panelists whose concern is primarily with improvement of health and alleviation of pollution.

B. Solid Standard Reference Materials to Check the Photometric Scale of Spectrophotometers - R. Mavrodineanu and J. R. Baldwin

The need for providing means and materials to check the proper functioning of a spectrophotometer was discussed in some detail in a previous publication [1]. At that time it was established that the accuracy of the photometric scale is critical, and the most demanding parameter in spectrophotometric measurements. Hence, particular attention was given to a number of ways for checking this parameter. Investigations have indicated that solid colored glass filters, exhibiting optical neutrality over the spectral range from 400.0 nm to 700.0 nm, would constitute an acceptable Standard Reference Material. From the various colored glass filters available, Schott NG 4 "neutral glass" was selected, prepared and characterized and is now being

issued as SRM 930. This standard consists of three filters each 25 mm long and 10 mm wide. They are about 1.0 mm, 1.5 mm and 2 mm thick and have nominal transmittances of 10, 20 and 30 percents, respectively. Each filter is mounted in a metal holder which fits the cell compartment of most conventional spectrophotometers; a set of three such filters is illustrated in figure 1. The provisional certificate

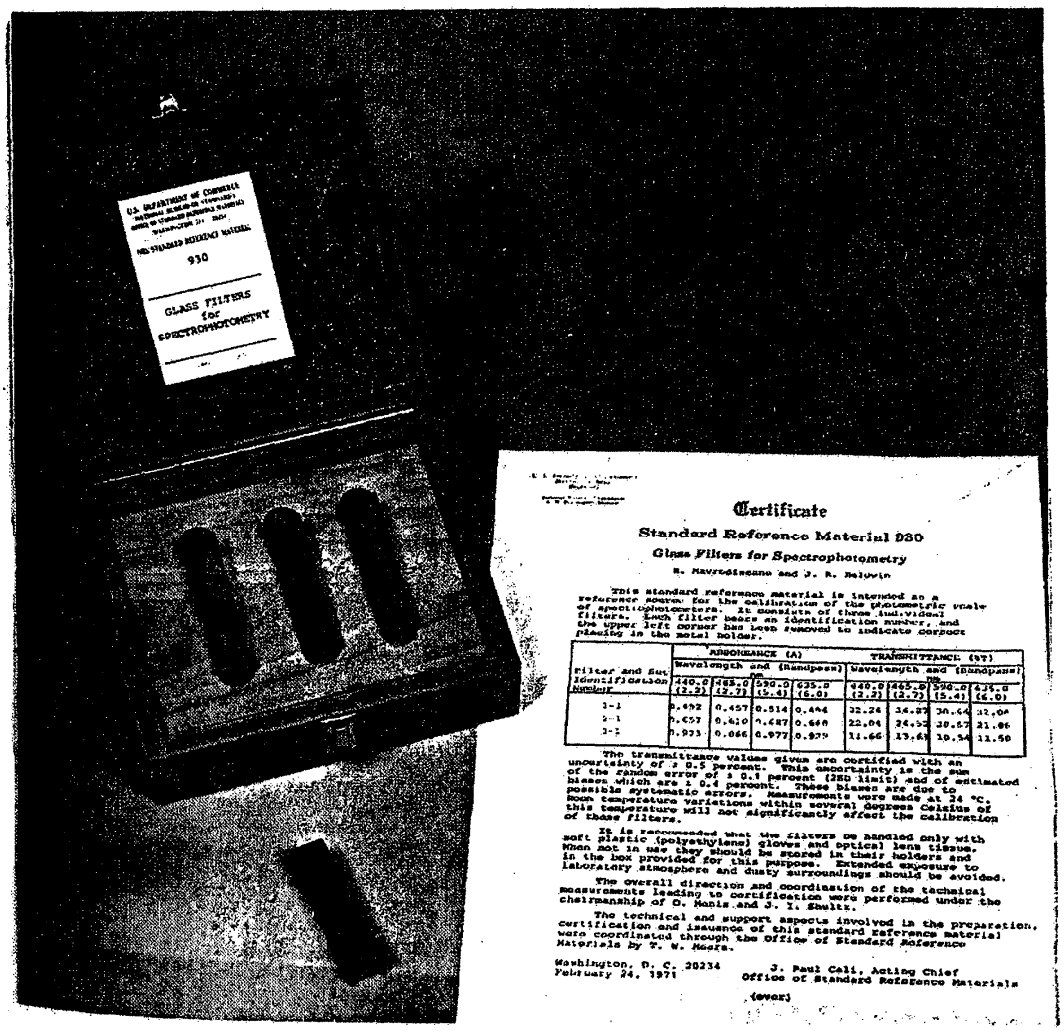


**Figure 1.** Set of three glass filters with the corresponding provisional certificate constituting SRM-930.

U. S. Department of Commerce
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# Certificate

## Standard Reference Material 930

### Glass Filters for Spectrophotometry

R. Mavrodineanu and J. R. Baldwin

This standard reference material is intended as a reference source for the calibration of the photometric scale of spectrophotometers. It consists of three individual filters. Each filter bears an identification number, and the upper left corner has been removed to indicate correct placing in the metal holder.

| Filter and Set Identification Number | ABSORBANCE (A) | | | | TRANSMITTANCE (%T) | | | |
|---|---|---|---|---|---|---|---|---|
| | Wavelength and (Bandpass) nm | | | | Wavelength and (Bandpass) nm | | | |
| | 440.0 (2.2) | 465.0 (2.7) | 590.0 (5.4) | 635.0 (6.0) | 440.0 (2.2) | 465.0 (2.7) | 590.0 (5.4) | 635.0 (6.0) |
| | | | | | | | | |

The transmittance values given are certified with a relative uncertainty of ± 0.5 percent (example: a nominal value of absorbance of 0.500 ± 0.0022). This uncertainty is the sum of the random error of ± 0.1 percent (2SD limit) and of estimated biases which are ± 0.4 percent. These biases are due to possible systematic errors. Measurements were made at 24 °C. Room temperature variations within several degrees Celsius of this temperature will not significantly affect the calibration of these filters.

It is recommended that the filters be handled only with soft plastic (polyethylene) gloves and optical lens tissue. When not in use they should be stored in their holders and in the box provided for this purpose. Extended exposure to laboratory atmosphere and dusty surroundings should be avoided.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of O. Menis and J. I. Shultz.

The technical and support aspects involved in the preparation, certification and issuance of this standard reference material were coordinated through the Office of Standard Reference Materials by T. W. Mears.

Washington, D. C. 20234
February 24, 1971

J. Paul Cali, Chief
Office of Standard Reference Materials

The transmittance measurements were made with a double-beam spectrophotometer containing a quartz double monochromator. The photometric scale of the instrument is divided into 1000 divisions, each division representing 0.1 percent transmittance. A corresponding absorbance scale is also provided on the instrument. The accuracy of the photometric scale was confirmed by the high-accuracy spectrophotometer designed and constructed at the National Bureau of Standards. The accuracy of this instrument was established by light-addition measurements.

The neutral NG-4 glass for the filters was provided by Schott of Mainz, Germany and is designated as "Jena Colored and Filter Glass." Nominal transmittance for a filter 1.5 mm thick is 20 percent at 400.0 nm wavelength and 32 percent at 700.0 nm wavelength. Between these limits the transmittance varies in a monotonous manner [1].

The filter holder and the size and shape of the filters were selected to conform to the dimensions of the sample compartment of most conventional spectrophotometers. The filters are approximately 1.0, 1.5, and 2.0 mm thick. Corresponding to these thicknesses are nominal transmittances of 30, 20, and 10 percent, respectively. These thicknesses were selected to provide a means for calibrating the photometric scale at three different levels.

The transmittance of filters depends on the intrinsic properties of the material. Spectral bandpass, wavelength [1,2], geometry of the optical beam, surface conditions, and positioning of the filter also affect the transmittance values, and can lead to further biases. The certified data will be reproduced when transmittance measurements are made under similar conditions. The effective spectral band passes used to determine the certified values are given on the face of the certificate.

Prior to the certification measurements, each filter was examined for surface defects and thoroughly cleaned. If, through handling, the surface of the filter becomes contaminated with dust, it may be cleaned with a small soft brush attached to a rubber tube connected to a vacuum source [3]. If the surface becomes contaminated with fingerprints, they must be eliminated before making measurements. This may be accomplished by removing the filter from its holder, breathing lightly on it, and rubbing the surface gently with optical lens tissue. The clean filter is then replaced in its proper position in its holder. To remove and replace the filter in the metal holder, the spring-loaded plate should be lifted with care to prevent damage to the filter. As little handling as possible is recommended.

NOTE: The check of the calibration of photometric scales defines only one of the parameters required for obtaining accurate transmittance values and molar absorptivities. Other factors that also must be established are wavelength accuracy, stray light, cell parameters, fluorescence, polarization, reflection, and temperature coefficient. Some of these variables are discussed in NBS Technical Notes [1]. It is planned to summarize various aspects of accurate spectrophotometric measurements in an NBS-260 Special Publication which would provide additional data on specific standard reference materials. In the interim, SRM 930, should be used as described in the certificate. Consult the manufacturer of the instrument if differences are obtained that exceed those specified by the manufacturer.

We wish to acknowledge the cooperation of George N. Bowers, Jr., M.D., of Hartford Hospital, Hartford, Connecticut; Royden N. Rand, Ph.D., of the Hospital of the University of Pennsylvania, Philadelphia, Pennsylvania; and Donald S. Young, M.B., Ph.D., of the National Institutes of Health, Bethesda, Maryland.

1. R. Mavrodineanu, Solid Materials to Check the Photometric Scale of Spectrophotometers, NBS Tech. Note 544, O. Menis and J. I. Shultz, ed., pp. 6-17, U. S. Government Printing Office, Washington, D. C. 20402 (Sept. 1970). ibid. NBS Tech. Note 584, 1971 (to be issued).

2. K. S. Gibson, Spectrophotometry, NBS Circ. 484, (Sept. 1949).

3. J. R. Edisbury, Practical Hints on Absorption Spectrophotometry, Plenum Press, New York (1967).

which accompanies these filters and which gives the absorbance and transmittance values together with certain information concerning the handling of the filters, is reproduced on pages 4 and 5.

1. Study of Surface Properties of Filters

The transmittance data given in the certificate depend not only on the intrinsic properties of the glass, but also on the surface condition of the glass. This parameter varies with time and exposure conditions. When glass is exposed to normal room atmosphere and temperature, its surface is corroded to an extent depending on the composition, time of exposure, concentration, temperature and nature of the glass surface and acting agents. This action produces a change in the reflecting and transmitting properties of the material [2, 3, 4]. For instance, one of the factors which can produce such changes is called "blooming" of the glass which is due to the formation of an SiO layer at the surface of the glass. This layer, which increases the transmittance, acts as an antireflection coating. The speed with which such a layer is formed varies with the composition of the glass, the atmosphere and time. Generally speaking, several years are needed for a fresh surface to reach an equilibrium. This and similar phenomena are presently being studied, along with means to stabilize the surface state of glass filters. Until more information is acquired in this field, we recommend that the colored glass filters be rechecked annually to determine whether any physico-chemical changes, which might affect the transmittance values, have occurred.

Another important factor is the need for a clean surface. Until now the final cleaning of the NG-4 filters was made with redistilled ethyl alcohol and pure water (thermally distilled and deionized). Other cleaning procedures are under consideration and the use of isopropyl alcohol in vapor or liquid form is being investigated [5].

2. Ultraviolet Region

The Schott NG-4 type glass now in use has a transmittance which is limited to the visible region of the spectrum. Since the ultraviolet region, from about 200 nm, is also important to the analyst who uses spectrophotometric methods, exploratory work is underway to select and certify solid materials for checking the photometric scale in this spectral region.

3. Cooperative Study of Colored Neutral Glass Filters

A cooperative study was carried out in collaboration with three clinical laboratories to determine the reproducibility of transmittance measurements on the Schott NG-4 neutral glass filters. Three filters having nominal transmittances of 10, 20 and 30 percent were measured at four wavelengths on a conventional spectrophotometer at the NBS. The same filters were then sent to laboratories A, B and C describing the technique to be used in measuring their transmittances. The results obtained are summarized in table 1 and include the percent transmittance (% T) values,

Table 1. Comparative % T measurements performed by four laboratories on three Schott NG-4 colored glass filters.

| Laboratory | | A | | | |
|---|---|---|---|---|---|
| Measurement | | % T | | | |
| No. | | 440 nm | 465 nm | 590 nm | 635 nm |
| 1 | Ave. | 12.91 | 14.99 | 11.68 | 12.71 |
| | S.D. | 0.0063 | 0.004 | 0.008 | 0.005 |
| | % S.D. | .049 | .027 | .070 | .041 |
| | Diff. % | - .4 | - .07 | - .6 | - .5 |
| 2 | Ave. | 19.61 | 22.37 | 19.06 | 20.50 |
| | S.D. | 0.004 | 0.010 | 0.004 | - |
| | % S.D. | .021 | .046 | .022 | - |
| | Diff. % | - .5 | - .3 | - .3 | -0.1 |
| 3 | Ave. | 32.81 | 35.44 | 31.12 | 32.58 |
| | S.D | 0.0080 | 0.0080 | 0.0050 | 0.0050 |
| | % S.D. | .023 | .023 | .017 | .016 |
| | Diff. % | + .3 | + .2 | + .1 | + .2 |

| Laboratory | | B | | | |
|---|---|---|---|---|---|
| Measurement | | % T | | | |
| No. | | 440 nm | 465 nm | 590 nm | 635 nm |
| 1 | Ave. | 12.91 | 14.87 | 11.56 | 12.59 |
| | S.D. | - | 0.041 | 0.041 | - |
| | % S.D. | - | .274 | .36 | - |
| | Diff. % | -0.4 | - .9 | -1.6 | -1.4 |
| 2 | Ave. | 19.59 | 22.39 | 18.90 | 20.51 |
| | S.D. | - | - | 0.053 | - |
| | % S.D. | - | - | .281 | - |
| | Diff. % | -0.6 | -0.2 | -1.1 | -0.05 |
| 3 | Ave. | 32.58 | 35.23 | 30.90 | 32.36 |
| | S.D. | - | 0.093 | - | - |
| | % S.D. | - | .264 | - | - |
| | Diff. % | -0.4 | - .3 | -0.6 | -0.4 |

| Laboratory | | C | | | |
|---|---|---|---|---|---|
| Measurement | | % T | | | |
| No. | | 440 nm | 465 nm | 590 nm | 635 nm |
| 1 | Ave. | 12.88 | 14.96 | 11.66 | 12.65 |
| | S.D. | - | 0.014 | 0.011 | 0.018 |
| | % S.D. | - | .09 | .09 | .15 |
| | Diff. % | -0.6 | - .3 | - .8 | - .9 |
| 2 | Ave. | 19.54 | 22.34 | 19.12 | 20.37 |
| | S.D. | - | - | 0.024 | - |
| | % S.D. | - | - | .13 | - |
| | Diff. % | -0.9 | -0.4 | + .5 | -0.7 |
| 3 | Ave. | 32.88 | 35.40 | 30.97 | 32.43 |
| | S.D. | - | - | - | - |
| | % S.D. | - | - | - | - |
| | Diff. % | +0.5 | +0.1 | -0.4 | -0.2 |

| Laboratory | | NBS | | | |
|---|---|---|---|---|---|
| Measurement | | % T | | | |
| No. | | 440 nm | 465 nm | 590 nm | 635 nm |
| 1 | Ave. | 12.96 | 15.00 | 11.75 | 12.77 |
| | S.D. | 0.0053 | 0.0037 | 0.0048 | 0.0057 |
| | % S.D. | .041 | .024 | .041 | .045 |
| | Diff. % | - | - | - | - |
| 2 | Ave. | 19.71 | 22.44 | 19.11 | 20.52 |
| | S.D. | 0.0049 | 0.0052 | 0.0038 | 0.0049 |
| | % S.D. | .025 | .023 | .020 | .024 |
| | Diff. % | - | - | - | - |
| 3 | Ave. | 32.72 | 35.35 | 31.09 | 32.50 |
| | S.D. | 0.0045 | 0.0056 | 0.0040 | 0.0043 |
| | % S.D. | .014 | .016 | .013 | .013 |
| | Diff. % | - | - | - | - |

the standard deviation (S. D.), the percent standard deviation (% S. D.), and the percent difference (% difference). This difference was calculated using the NBS data as a reference.

In this study, the cooperation of George N. Bowers, Jr., M. D., of Hartford Hospital, Hartford, Connecticut, Royden N. Rand, Ph.D., of the Hospital of the University of Pennsylvania, Philadelphia, Pennsylvania, and Donald S. Young, M.D., Ph.D., of the National Institutes of Health, Bethesda, Maryland is gratefully acknowledged.

C. Instrument Development - R. Mavrodineanu

The decision to provide solid and liquid filters to check the photometric scale of spectrophotometers implicitly required that the certified transmittance data assigned to these filters be given with a known accuracy.

Since conventional spectrophotometers cannot readily provide such information, the design and construction of a research instrument on which transmittance data could be measured with known accuracy was initiated. After a comprehensive examination of the existing literature

in this field, (Ref. 6 to 34 arranged in chronological order) a decision was made to construct an instrument similar in design to the instrument at the National Physical Laboratories (NPL), Teddington, England, where a long tradition in high accuracy spectrophotometry exists. A visit was arranged with Dr. Frank J. J. Clarke, Head of Colorimetry and Photometry Section, Metrology Centre at NPL. During this visit, the NPL high accuracy spectrophotometer was examined in detail and work was performed with the instrument. Furthermore, detailed discussions with Dr. Clarke and his associates, Mr. G. Lambert and Anne Compton, provided valuable scientific information for use in our work.

1. Description of the NBS Instrument

The NBS high accuracy spectrophotometer is a single beam instrument which contains the following elements: (A) a constant light source, (B) a monochromator, (C) a sample holder, (D) a system to check the accuracy of the photometric data and (E) an integrating sphere attached to a photomultiplier - digital voltmeter unit. Figure 2 illustrates

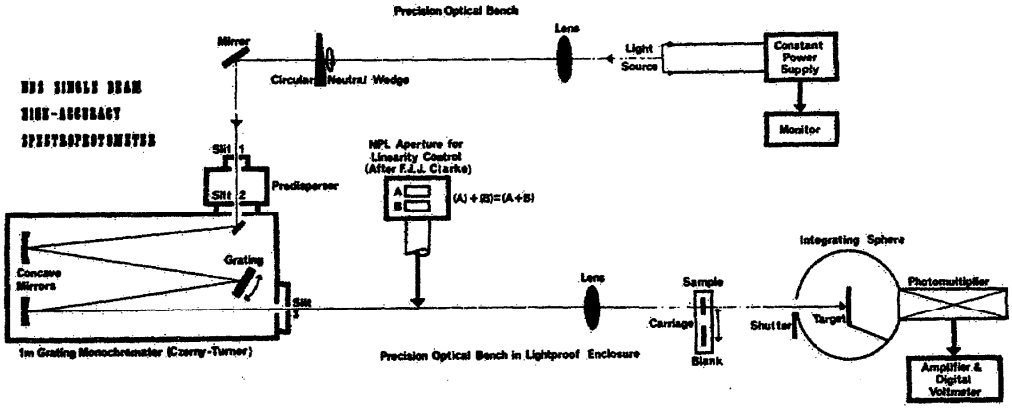


Figure 2. Schematic description of the NBS high accuracy spectrophotometer.

schematically the arrangement of these various components. A neutral wedge is placed after the light source to select various levels of radiation intensities required for measurements. A description of the components is presented in the following sections.

a. The Light Source. Since the instrument is a single beam type it is essential that the radiation source be constant and homogeneous. Additional desirable conditions are: (1) capability of monitoring the current supplied to the source and (2) black-body type radiation. The source which was selected was designed and used at NBS by H. J. Kostkowski and R. D. Lee of the Institute for Basic Standards in their radiation studies. This source was duplicated in our instrument with considerable assistance from its developers.

The source consists of a tungsten incandescent filament lamp and includes a tungsten ribbon 8 mm x 2 mm. The current used to operate this lamp at approximately 3000 °K is 6 V and 18 amp; our source is operated at 5 V and 13 amp. The power supply is capable of delivering 15 V and 50 amp, when operated in the constant current mode. To achieve this mode of operation, an external sensing resistor of 0.1 Ω and 50 amp and a current control circuit is placed in series with the supply. A feedback across this resistor is connected to the power supply sensing system. The characteristic of this operation is the ability to automatically change its output voltage so as to maintain a constant current to the load resistor, which, in our case, is the lamp source. The nominal current regulation obtained is better than 0.01 percent and the stability over an 8 hour period, at constant load temperature, is better than 0.02 percent. The stability of the current delivered to the lamp is monitored with a high accuracy potentiometer having a range from 0 to 1.6110 V to 0 to 0.16110 V and a corresponding limit of error of $\pm$ 0.01 percent $\pm$ 20 μV to 0.015 percent

± 0.5 μV. This potentiometer is used in conjunction with a null meter which is sensitive to variations in the current supplied to the lamp from 1 part in 1000 to 1 part in 1,000,000 per division. The potentiometer is connected to the current source across a resistor of 0.01 Ω and 100 amp, and placed in series with the lamp.

The demagnified (2 to 1) image of the ribbon filament is projected on the entrance slit of the predisperser by a glass achromate whose focal distance is 254 mm and diameter is 44 mm. This achromate, as well as the other two achromates used in the optical system, was calculated and selected by K. Mielenz, of the Institute for Basic Standards. A circular neutral wedge is placed between the light source and the predisperser. This wedge, evaporated Inconel on a glass disk (150 mm diam.), is linear in density and provides a light attenuation of 100 to 1. The wedge can be rotated by an electrical motor (1 rev. per sec) to select proper radiation intensity levels as required by the measurements.

b. The Monochromator. The monochromator is a 1-m Czerny-Turner type grating instrument. The flat grating has 1200 grooves per mm over a surface of 100 x 100 mm. The monochromator is provided with a predispersing attachment to reduce the stray light. This predisperser is a small quartz prism monochromator connected to the scanning system of the 1-m instrument. According to the data provided by the manufacturer, the stray light of the predisperser-monochromator unit is less than 1 part in 10,000,000. A wavelength counter permits readings to 1 Å and the scanning speed can be varied from 0.5 to 2000 Å/min through a 12 speed synchronous electric motor.

The optical components are placed on precision lathe-bed type optical benches, 120 and 160 cm long, and are equipped with appropriate carriers provided with x-y-z adjustments.

c. Sample Carrying Unit. The sample carrying unit consists of a platform provided with two holders which can accept 3/4 in. rods and a variety of sample supports. These holders can be moved laterally through a rack and pinion arrangement. The platform is mounted on 4 ball bushings which run on two horizontal rods and can be moved pneumatically across the optical axis. The use of a pneumatically operated motion was recommended by G. E. Moore and J. T. Sterling of the Institute for Applied Technology and by L. Owen. The total travel is 8 in. and the linear movement is smooth. The position of the platform can be reproduced within 0.025 mm. This unit is illustrated in figure 3 and is located between the two achromates. The sample holder is designed to accept conventional solid or liquid filter holders which fit most spectrophotometers. The holders are provided with a thermostated jacket.

d. System to Check the Accuracy of the Photometric Reading. Since the high accuracy spectrophotometer is single beam, accurate photometric data are obtained when there is a linear relation between the radiation flux and the corresponding response of the photodetector.

Linearity of photodetectors can be measured by several means: the inverse square law [8, 16], the use of optical elements having a known transmittance which can be determined by other means [18] and the light addition principle using a plurality of light sources [6, 7, 9, 10, 11, 14, 19, 20, 21, 29, 32, 33, 34] or multiple apertures [12, 13, 15, 17, 22, 24, 26, 27, 28, 31]. A novel approach to the problem of accurate photometric measurements was described by O. C. Jones and F. J. J. Clarke [25, 30]. A critical discussion of some aspects of accurate spectrophotometry will be found in an NBS manuscript by Gibson and Associates [23]. The light addition principle, using two apertures with one source of radiation, was chosen in our work. The aperture method for checking the linearity of photometric data was used in 1936 at the

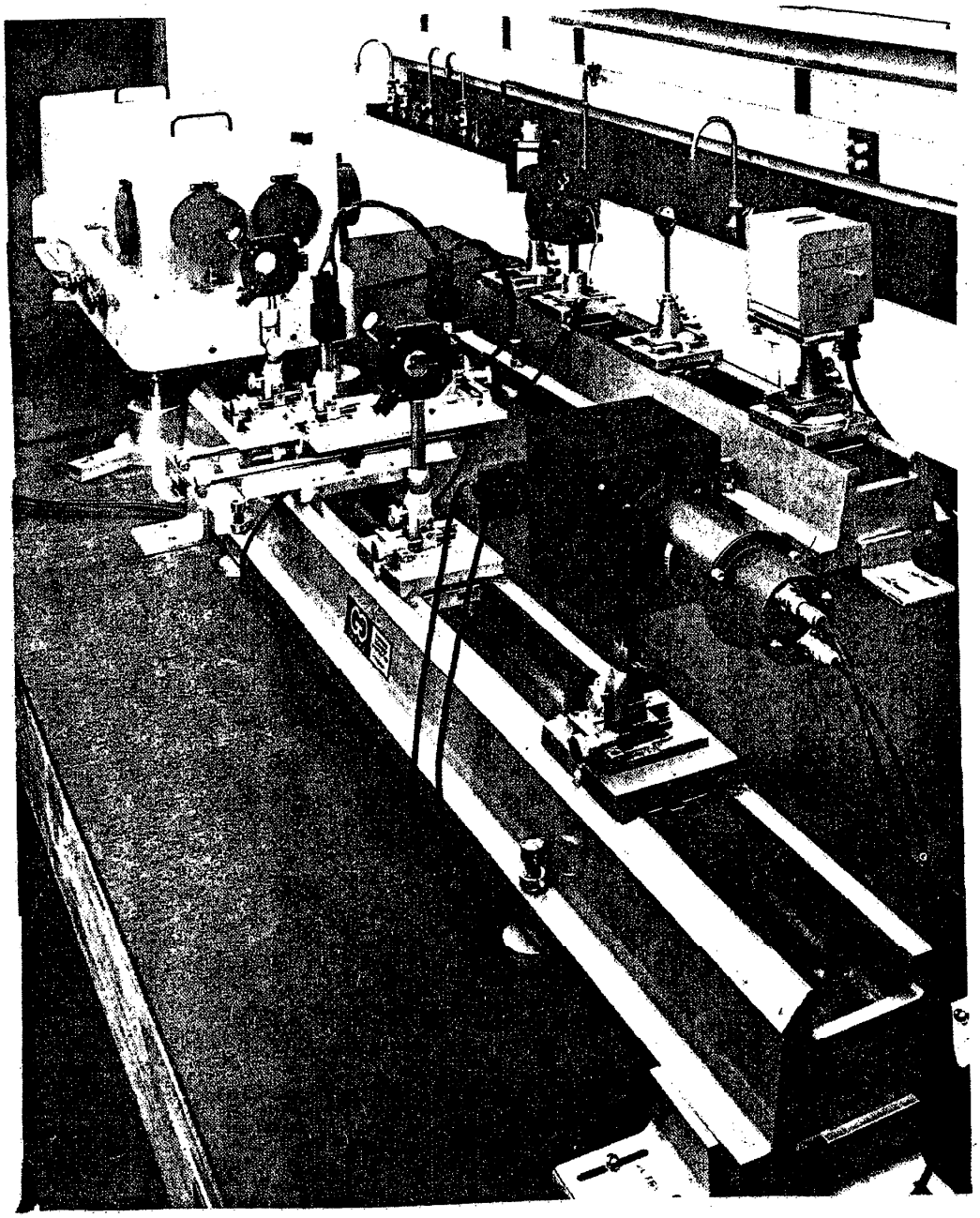

Figure 3. NBS high accuracy spectrophotometer. At right, the light source, at upper left, the 1m monochromator The optical bench at the exit slit of the monochromator carries an achromate; the sample platform; a second achromate followed by the integrating sphere and photomultiplier assembly.

NPL by Preston and Cuckow [12] in conjunction with a single beam spectrophotometer, employing a five-aperture screen. One year later, Buchmüller and König [13] described and used, among others, a two-aperture unit. At NBS, Barbrow [15] used a ten-aperture arrangement, while Harding [17] and Cordle and Habell [26] at the NPL described a two-aperture system. Multiapertures were used by Hoppman [22], Bischoff [24], Sanders [27] and Nonaka and Kashima [28]. Finally, Clarke [31] discussed in detail the use of a two-aperture system to check the accuracy of photometric data obtained on his spectrophotometer at NPL. It is this system which was reproduced and used at NBS.

The two-aperture unit consists of a metal plate (130 mm by 100 mm) containing 2 rectangular windows, A and B, (20 mm by 8 mm) located one above the other. Each aperture can be closed by a light-tight shutter which is operated pneumatically by remote control. The aperture plate is placed in the optical path after the exit slit of the monochromator and within the optical solid angle of the instrument. The image of the apertures is then projected on the target of the integrating sphere. A glass achromate with a focal distance of 190 mm and a diameter of 60 mm is used for this purpose. The arrangement is illustrated in figure 4. No optical element should be placed between the aperture plate and the monochromator. The linearity check consists of measuring the photocurrent produced when aperture A is open, then closed and then aperture B is open and then closed. The value of A + B is then compared with the values obtained with both apertures (A + B) open. If the system is linear (or accurate) these two values should be identical:

$$(A) + (B) \equiv (A + B)$$

If this is not the case, the system shows nonlinearity which is proportional to the amount by which the sum of

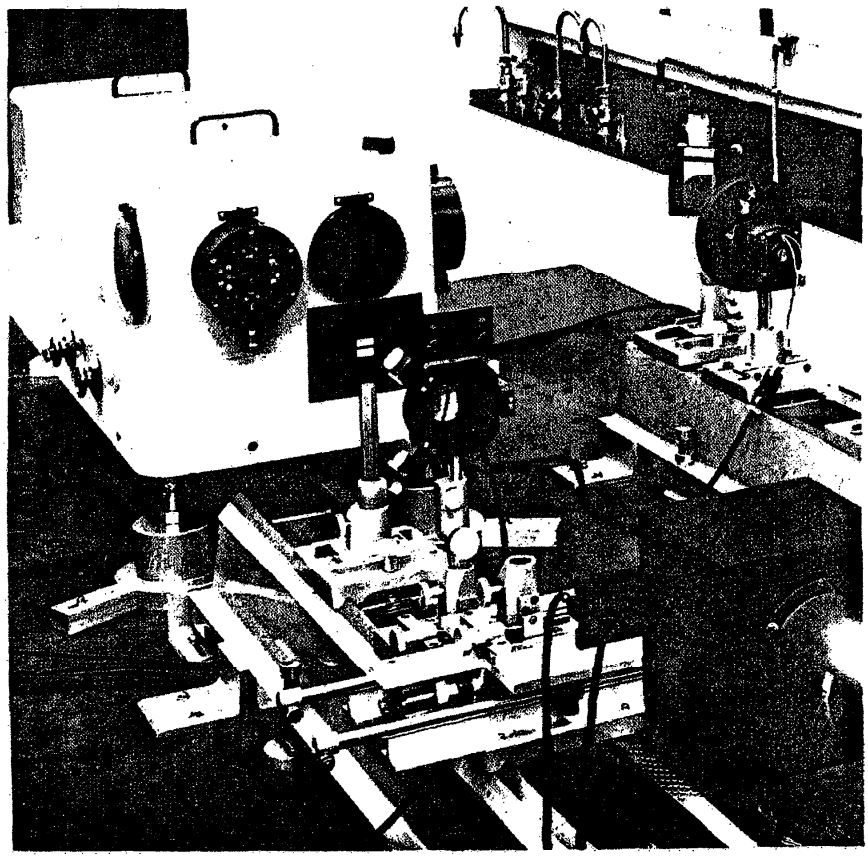

Figure 4. NBS high accuracy spectrophotometer. Same arrangement as in figure 3 except for the aperture system which is now placed after the exit slit of the monochromator. This arrangement is used when making linearity measurements.

(A) + (B) differs from (A + B). This difference is then used to correct the transmittance values measured on the solid or liquid filters.

e. Integrating Sphere and Photomultiplier Arrangement. Radiations are passed through the aperture or the filter and are then received on the target of the integrating sphere. This sphere is illustrated in figures 3 and 4. A rectangular block of aluminum made from identical halves was cut to produce a half sphere in each half block. Then the halves were joined together to form the hollow sphere. Its

diameter is 125 mm. A target made from a circular plate 35 mm in diameter, is located at the center of the sphere. The front surface of the sphere has a 20 mm diameter entrance opening which can be closed by a shutter that is operated remotely by a pneumatic system. A 50 mm diameter opening is at the opposite end to which the housing of the photomultiplier is attached by an "O" ring to provide a light-tight joint. The inside of the sphere is coated with a suspension of $BaSO_4$; the outside is painted black (1 percent reflection).

The photomultiplier is a 50 mm flat-faced, end quartz window tube with a 44 mm cathode and 11 venetian blind dynodes having CsSb secondary emitting surfaces. The cathode is identified as S-20 or tri-alkali type. The spectral range of this tube is from below 200.0 nm to 850.0 nm. The operating voltage is 850 V. The photomultiplier output is supplied to an operational amplifier and a series of high precision resistors rated at $10^6$, $3 \times 10^6$, $10^7$, $3 \times 10^7$ and $10^8$ Ω. A dark current compensation is also available. The output from the amplifier-resistors unit is supplied to a $10^{-5}$ V digital voltmeter. This electronic system was designed and assembled at NBS by R. J. Carpenter and K. W. Yee.

The optical components located after the exit slit of the monochromator, including the photomultiplier tube, are enclosed in a light-tight box 200 cm long, 70 cm wide and 76 cm deep. The front panel, which is removable, is provided with a sliding door to permit rapid access to the filter-holder system. The box contains outlets for the compressed air which operates the apertures, sample carriage and integrating sphere shutter, and the electrical connection from the photomultiplier. The inside walls are lined with thermal insulation painted black. When in use, all non-black metal parts are covered with a black cloth to reduce stray light.

D. Experimental Results

The stability of the electronic system was determined with a tritium-activated phosphor. Because tritium has a long half-life (12.5 years), the light output is considered stable. This source was placed in front of the integrating sphere and four series of 20 measurements each were made. The average values obtained over a 10 min period were: $1.1340_2$ V; $1.1342_1$ V; $1.1342_0$ V; $1.1342_2$ V. From these values it can be concluded that the stability of the photomultiplier tube, with its electronics, is better than 1 part in 10,000. When the ribbon filament lamp was used after a 2 hour warm-up, the measurements indicated a stability of several parts in 10,000.

The linearity of photometric data is a function of the photomultiplier, the voltage supplied, the load resistor and the amplifier. The wavelength at which the measurements are made is not critical.

A series of linearity measurements were made using 850 V at the photomultiplier and the $3 \times 10^6$ Ω resistor. The results, expressed as a percent correction of the transmittance percent, indicate that a correction of -0.15 should be made at 50 percent transmittance, -0.22 at 25 percent transmittance, and -0.26 at 12.5 and 6.25 percent transmittance values. Interpolation between these values provides the correction at other transmittance values. In our work, linearity measurements were made at a wavelength of 560.0 nm. A series of transmittance measurements were made on three Schott NG-4 filters having nominal transmittances of 10, 20 and 30 percent. The optical arrangement used for the measurements is described in figure 3. The image of the exit slit (about 10 mm by 1.5 mm) was projected at the surface of the filter and in its center. After passing through the filter, the radiations are projected on the target of the integrating sphere. The other parameters,

such as photomultiplier voltage, resistor value, amplifier gain, and light source output, were the same as those used in the linearity measurements.

The transmittance measurements are made by determining the average voltage reading by the digital voltmeter which corresponds to the unattenuated radiation intensity, $I_o$, and corresponding to the attenuated radiation after passing through the filter, I. The ratio $\frac{I}{I_o}$ is the uncorrected transmittance of the filter at the selected wavelength. To minimize the inevitable variations during the measurements, a successive series of Io and I data are collected, averaged and ratioed. Such a series of data is illustrated in table 2. These transmittance measure-

Table 2. Transmittance measurements on a Schott NG-4 glass filter with the NBS high accuracy spectrophotometer.

Temperature = 23.50 °C

| Wavelength nm | $I_o$ | I | $I_o$ | I | $I_o$ |
|---|---|---|---|---|---|
| 440.0 | 2.0030 | 0.6620 | 2.0010 | 0.6620 | 2.0010 |
| | 2.0015 | .6625 | 2.0028 | .6630 | 2.0045 |
| 465.0 | 2.0040 | .7156 | 2.0022 | .7150 | 2.0015 |
| | 2.0050 | .7150 | 2.0015 | .7160 | 2.0045 |
| 590.0 | 2.0028 | .6274 | 2.0047 | .6282 | 2.0067 |
| | 2.0048 | .6275 | 2.0028 | .6270 | 2.0050 |
| 635.0 | 2.0060 | .6570 | 2.0070 | .6573 | 2.0080 |
| | 2.0055 | .6568 | 2.0068 | .6570 | 2.0080 |

| | Average $I_o$ | Average I | % T uncorrected | % T corrected |
|---|---|---|---|---|
| 440.0 | 2.0023 | 0.6624 | 33.08 | 32.99 |
| 465.0 | 2.0031 | .7154 | 35.71 | 35.62 |
| 590.0 | 2.0045 | .6275 | 31.30 | 31.21 |
| 635.0 | 2.0069 | .6570 | 32.74 | 32.65 |

ments were repeated over a period of several weeks, using the same three filters. The summary of the results is given in table 3. Another series of transmittance measurements was made using another NG-4 filter whose nominal transmittance is 30 percent. The results were compared with similar measurements made on a conventional spectrophotometer (see table 4). An average bias of + $0.23_5$ relative percent was found.

Table 3. Repeatability of % T measurements performed with the NBS high accuracy spectrophotometer on three colored glass filters.

| Wavelength nm | Filter 10 % T | | | Filter 20 % T | | | Filter 30 % T | | |
|---|---|---|---|---|---|---|---|---|---|
| 440.0 | 11.62 | 11.62 | 11.62 | 19.83 | 19.82 | 19.91 | 32.98 | 32.97 | 32.99 |
| 465.0 | 13.57 | 13.58 | 11.60 | 22.63 | 22.59 | 22.69 | 35.66 | 35.67 | 35.62 |
| 590.0 | 10.38 | 10.38 | 10.39 | 19.16 | 19.16 | 19.27 | 31.19 | 31.18 | 31.21 |
| 635.0 | 11.37 | 11.31 | 11.40 | 20.58 | 20.60 | 20.71 | 32.61 | 32.61 | 32.65 |

| | Averages | Averages | Averages |
|---|---|---|---|
| 440.0 | 11.62 | 19.85 | 32.98 |
| 465.0 | 13.58 | 22.63 | 35.65 |
| 590.0 | 10.38 | 19.20 | 31.19 |
| 635.0 | 11.36 | 20.63 | 32.62 |

Table 4. Comparison of % T measurements performed on a Schott NG-4 filter using the NBS high accuracy instrument and a conventional spectrophotometer provided with a quartz prism double monochromator in a double beam arrangement.

| Wavelength nm | NBS Instrument | Conventional Instrument | Diff. | Relative % Diff. | Average Relative % Diff. |
|---|---|---|---|---|---|
| 440.0 | 32.82 | 32.75 | +0.07 | +0.20 | |
| 465.0 | 35.51 | 35.40 | + .11 | + .30 | +$0.23_5$ |
| 590.0 | 30.98 | 30.93 | + .05 | + .16 | |
| 635.0 | 32.38 | 32.32 | + .06 | + .18 | |

The data on the high accuracy spectrophotometer at NPL, as well as at NBS, are made by visual averaging and manual transfer. Such a method has bias which depends, among others, on the experience of the operator. This type of bias can be eliminated if the data acquisition is made through a computer interfaced with the digital voltmeter. In this manner many readings can be taken over a predetermined time interval and then averaged. A statistical evaluation of each set of results can also be obtained simultaneously. The design of such a computer data system was completed and the hardware procured. The use of this non-bias procedure to acquire and process the information given by the NBS high accuracy spectrophotometer was started during the early part of 1971.

The optical components used in the present instrument are made of glass. This initial choice limits the use of the instrument to the visible part of the spectrum (380.0 nm to 800.0 nm). This spectral range will be extended to the ultraviolet region by providing a quartz optical system.

E. Studies of Liquid Filters as Potential Absorbance Standards - R. W. Burke and E. R. Deardorff

A program involving the investigation of various liquid filters as potential absorbance standards was described in NBS Technical Note 544 [1]. Three types of filters were identified: (1) individual solutions of inorganic salts, (2) composite mixtures and (3) solutions of inorganic dyes. During the past year, additional studies were undertaken on each type of filter.

1. Solutions of Inorganic Salts

The need for ultraviolet absorbance standards, especially by clinical chemists, resulted in a critical investigation of the acidic potassium dichromate system. The results of this study are described in a subsequent section of this report.